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(54) Method for reparative enamelling of defects in stove-enamels with powdered lacquers

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(56) Oppositions
DE 38 33 225 A1
K. Bär: Sekundenschnelle Aushärtung von Pulverlacken [Hardening, within seconds, of a powdered lacquer], JOT 1998/2, pp. 26-29

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(57) Method for the reparative enamelling of defects in stove-enamels, in which the defect, which has been readied for reparative enamelling is coated with a powdered lacquer* coating

* ["Enamel" and "lacquer" are used interchangeably in the German document.]

agent or an aqueous powdered lacquer slurry, with the powdered lacquer then being melted and hardened by radiation with near infrared radiation (NIR).
The following declarations are from gathered documents submitted by the applicant for examination according to Section 44 of the Patent Law.

Description
The invention relates to reparative enamelling of defects within stove coating layers with powder a coating agent.

Enamelling defects, such as, pits, depressions, scratches, or dirt inclusions within stove coating layers, for example, within stove coating layers made from powder enamels, can be repaired with liquid enamels. The repair process is time consuming and labor intensive. For example, the hardening of the reparative enamel requires exposure to high temperatures for a sufficiently long period of time. If the substrates to undergo reparative enamelling are heat sensitive, then the temperature of the object cannot be chosen to be as high as desired. If the substrates that must undergo reparative enamelling are made from a mixture of heat-sensitive and heat-resistant components, one generally proceeds by removing the temperature-sensitive components before the thermal treatment, then one again adds those components. These measures constitute obstacles in, and they increase the cost of, series enamelling processes in particular, for example, the enamel of cars with filler, covering, or clear lacquers.

A special problem in the reparative enamel of exterior, visible covering stove-enamels prepared from powdered lacquers is that the reparative enamelling has to be carried out in such a manner that the repaired place is not visible, for example, in so far as matching the hue or brilliance is concerned. In the case of the repair of stove-enamel powder clear lacquer coatings, there should also be no resulting difference in the refractive indexes of the stove-enamel powder clear lacquers and the hardened reparative clear lacquer.

Methods for the repair of defects in lacquer coatings are known, which avoid the usual thermal hardening by convection or conventional IR radiation, from DE-A-38 33 225, DE-A-197 20 894 and DE-A-197 20 946. The methods described therein use laser light as an energy source for hardening the reparative lacquer.

From EP-A-0 842 710, a method is known for repairing defects in powdered lacquer coatings, in which one places a filler body in the defect, which has been prepared for the repair, for example, by polishing or milling, then one bonds it with the defect. It is preferred for the filler body to match the dimensions of the prepared defect. EP-A-0 887 118 improves the methods known from EP-A-0 842 710 as far as the achieved quality is concerned, by carrying out the method of EP-A-0 842 710 in such a manner that the connection between the filler body and the defect is made under pressure. The methods of EP-A-0 842 710 and EP-A-0 887 118

prevent the drawbacks of repairing defects in the powdered lacquer coatings by means of liquid lacquers; however, they are expensive because of the requirement to prepare the filler bodies, especially to match the defects to be prepared.

In the contribution "Hardening, within seconds, of a powdered lacquer" (Kai Bär, JOT 2/98, pp. 26-29), a description is provided showing that the powdered lacquers can be hardened using near infrared radiation (NIR) of high intensity, without any substantial heating of the substrate. The NIR technology allows the melting and hardening of the powdered lacquer coatings in a single processing step.

The problem of the invention is to provide an improved method for the reparative enamelling of defects in stove-enamels, in particular using stove-enamels prepared from powdered lacquers, which prevents the drawbacks of the art described in the prior art. The method is intended to be particularly well suited for an improvement of the enamel of series lacquered, industrially manufactured objects, in particular cars and car parts, for example, in the context of, or following, series enamelling.

The objective of the invention is thus a method for the reparative enamelling of defects in stove-enamels, in which the defect which has been readied for reparative enamelling is coated with a powdered lacquer coating agent or an aqueous powdered lacquer slurry, with the powdered lacquer then being melted and hardened by radiation with near infrared radiation (NIR).

In the method according to the invention, one or more defects are repair-lacquered within a stove-enamel, in particular within stove-enamel that has been applied using a powdered lacquer coating agent. The stove-enamels that can have defects can be, for example, single layer covering enamels or lacquer layers arranged within a multilayered enamel, for example base coats or filler layers, preferably exterior, visible, and color or effect producing lacquer layers, in particular transparent cover lacquer layers. It is preferred to use the method according to the invention for repairing defects within covering layers that have been stoved and consist of powdered lacquers, in particular clear powdered lacquers. It is particularly preferred to use the method according to the invention for repairing defects within stove-enamels that have been applied to cars or car parts.

The term "defects" refers to locally delimited defective places, for example, having a surface area of up to several square centimeters [sic], for example, 1 mm^2 to 100 cm^2, within a stove-enamel. The defects can be, for example, scratches, such as scratches made during assembly, or coating defects such as pits and depressions, or dirt inclusions.

It should be noted that the powdered lacquer coatings used for reparative enamelling include aqueous preparations of powdered lacquer coating agents, so-called aqueous powdered

lacquer slurries. However, in the method according to the invention, it is preferred to use the powdered lacquers themselves.

The powdered lacquers that are used in the method according to the invention as reparative lacquers contain a heat-hardenable self-crosslinking or other crosslinking binder system, preferably a foreign crosslinking binder/hardener combination. The term binder denotes the film-forming high-molecular-weight component of a duroplastic powdered lacquer, which in general constitutes at least 50 wt% of the base binder/hardener combination, while the hardener component in general is at most 50 wt% of this combination. The binder base is in principle not subject to any restrictions. For example, the binders that are conventionally used for powdered lacquers are suitable. Examples are: polyester resins, (meth)acrylic copolymers, epoxide resins, phenol resins, polyurethane resins, and siloxane resins. The binders have, for example, glass transition temperatures of 30-120°C, preferably less than 90°C, and they have, for example, number-average molecular weights (Mn) of 500-20,000, preferably less than 10,000; the hardeners have, for example, number-average molecular weights (Mn) of 84-3000, preferably less than 2000. It is possible to mix different binders and hardeners.

The binders and hardeners carry mutually complementary functional groups, that allow a thermal crosslinking reaction of the powdered lacquer to take place, for example, condensation reactions and/or addition reactions. Examples of such functional groups are carboxyl groups, epoxide groups, aliphatically or aromatically bound hydroxyl groups, isocyanate groups, blocked isocyanated groups, anhydride groups, primary or secondary amino groups, blocked amino groups, N-heterocyclic groups that are capable of ring-opening addition, such as oxazoline groups, (meth)acryloyl groups, and CH acid groups such as acetoacetate groups.

The person skilled in the art is familiar with the selection of mutually reacting groups. It is possible, optionally, to combine different reactive groups with each other. This can be achieved by means of binders that have different functional groups, or mixtures of different hardeners and/or binders are used.

The different functional groups can be present at the same time as the binder and/or hardener. The binders as well as the hardeners on average contain at least 2 functional groups per molecule. The ratio of binder to hardener in general is 98:2 to 50:50. It is preferably between 95:5 and 70:30.

Examples of the binder/hardener system that is conventionally used in powdered lacquers are polyester resins with low-molecular-weight epoxide or hydroxyl alkyl amide hardeners, epoxy/polyester hybrid systems, epoxy resins with dicyandiamide hardeners, carboxylic acid hardeners or phenol hardeners, hydroxyl functional polyesters or (meth)acrylic polymers with blocked polyisocyanates, and epoxide functional (meth)acryl copolymers with carboxylic acid or carboxylic acid anhydride hardeners.

In particular, in the case of the repair of defects in exterior, visible, stoved clear lacquer coatings, as reparative lacquers one uses, in the method according to the invention, powdered lacquers that contain, as binders, epoxide functional (meth)acrylic copolymers, in particular glycidyl(meth)acrylate copolymers with an epoxide equivalent weight of 250-700, and, as the hardener, one or more low-molecular-weight and/or polymer compounds having on average of 2 or more carboxyl functions per molecule and/or anhydrides thereof. Preferred hardeners are solid aliphatic dicarboxylic acids and/or their anhyrides, such as, in particular, dodecane dicarboxylic acid, which can also be used in a mixture with carboxy functional polyesters.

The powdered lacquers used according to the invention can contain conventional powdered lacquer additives in the conventional quantitative proportions of, for example, 0.1-5 wt%. Examples of such additives are leveling agents, degassing agents such as benzoin, antioxidants, light protection agents, matting agents, color-or effect-producing inorganic and/or organic pigments and/or filers, dyes, adhesives, lubricants, and catalysts as well as rheology controlling agents.

If covering pigments or "effect" pigments are used, they consist of powdered lacquer covering agents that are usable for repairing defects in color-or effect-producing lacquer layers. If no pigments or colorless pigments, for example, micronized titanium dioxide or silicone dioxide, are used, they generally are powdered lacquer covering agents that are useable for repairing defects in clear lacquer layers.

The manufacture of the powdered lacquer used a reparative lacquer in the method of the invention can be carried out by the usual methods for manufacturing powdered lacquers, for example, by extrusion of the finished powdered lacquer formulated by the dry mixing of all the required components, in the form of a pasty slurry, cooling of the slurry, coarse crushing, fine milling, and optionally followed by sieving to the desired particle size, for example, to mean particle sizes of 10-90 μm.

The method according to the invention can by carried out using fine particles of powdered lacquer, for example, with mean particle sizes of 1-40 μm. Fine particles of powdered lacquer or powdered lacquer fine grains can be manufactured in a targeted manner, however, it is produced as a material that in itself is not desired [sic], for example, during the powdered lacquer manufacture or the powdered lacquer application, and can thus be used advantageously in the method according to the invention.

The powdered lacquers can also be used as aqueous powder lacquer slurries. For this purpose, they can be converted, for example, by drying or wet milling, or by intensive dispersion of a powdered lacquer solution in water to an aqueous powdered lacquer slurry, from which one can optionally remove the organic solvent by distillation.

It is preferred for the powdered lacquers used in the method according to the invention to have the same solid-matter composition as the lacquer used for the preparation of the stove-enamel layer that has defects to be repaired. The repair preferably applies to defects in stove powdered lacquer layers [stove-enamel powdered layers]. In the process, both in the first enamelling and in the reparative enamelling according to the invention, powdered lacquers with identical compositions are used. This is particularly advantageous in repairing defects in exterior, visible, stoved clear lacquer layers. For example, the intrinsic color and the refractive index of the first enamel and of the reparative enamel then do not differ from each other.

In the method according to the invention, one repairs defects in a stove-enamel, using powdered lacquers as reparative lacquer. The defects may be ready for [application of] immediate reparative enamel, or they are prepared for said reparative enamel, for example, by polishing, milling, or working the repair sites with a laser. In general, the defects are at least cleaned before the powdered reparative lacquer is applied. In addition, it is advantageous to protect the defect-free surface portions of the surface before removing dirt, for example, by covering, placing an adhesive film, or the application of a stripping lacquer around the defects to be repaired.

The defects, which have been readied for reparative enamel, independently of whether they are on horizontal or vertical surfaces, can be coated with the powdered lacquer coating agent, for example, by mechanical means, such as by application by scattering, brushing, or painting, or the application may be carried out by spraying with the application installations conventionally used for that purpose. The application spraying can be supported, for example, electrostatically, such as with the use of corona or tribo spray devices.

In the method according to the invention, after the application of the powdered lacquer or after the application and drying of the aqueous powdered lacquer slurry, the powdered lacquer composition applied onto the defect is melted and hardened by NIR radiation, preferably with NIR radiation of high intensity. The NIR radiation is short-wavelength infrared radiation in the wavelength range of approximately 760-1500 nm, preferably 760-1200 nm. Radiation sources for NIR radiation are, for example, conventional high energy NIR emitters that can emit radiation with surface, line, or point-shaped focusing. Such NIR emitters are available commercially (for example, from the Industrie SerVis Company). For example, one can use high-performance halogen emitters with a radiation density of generally more than 1 W/cm^2, preferably more than 10 W/cm^2, and up to, for example, 15 MW/m^2. The emitters, for example, reach an emitter-surface temperature (glowing spiral temperature) of 2000-3000 K. Suitable emitters present, for example, an emission spectrum with a maximum of 750-1200 nm.

The radiation time in the method according to the invention is 1-300 sec, for example. During the radiation, the powdered lacquer applied to improve the defect melts and hardens, for example, within 1-300 sec, preferably within 5-60 sec.

The radiation can be carried out with a band installation equipped with one or more NIR emitters, or with an NIR emitter placed in front of the irradiated object or positioned at the site to be irradiated.

The first mentioned possibility is available, for example, for the reparative enamelling of individual parts or objects, wherein several defects are to be repaired in one step. In the process, the band speed and thus the duration of radiation can be varied. For example, band speeds of 1-7 m/min can be set, which can correspond to radiation times of 2-20 sec. The separation between the NIR emitter and the object surface can be, for example, 1-60 cm, preferably 4-20 cm.

In the second possibility, the NIR emitter is positioned in front of the object to be irradiated or the place to be irradiated. The duration of radiation can be, for example, 1-300 sec, and the object distance can be, for example, 1-60 cm, preferably 4-20 cm.

The different radiation parameters, such as band speed or duration of radiation, object distance, and radiation power of the NIR emitter used, can be adapted by the person skilled in the art to the requirements of a given repair problem.

It is also possible to use, for the hardening, a combination of NIR radiation and heat by convection-based heat sources, such as convection ovens or conventional long-wavelength infrared emitters.

After the hardening by NIR radiation of the powdered lacquer used to improve the defects, it can be advantageous to smoothen the repaired site, for example, by polishing.
Using the method according to the invention, defects can be repaired by single-layered stove-enamels. Is it also possible to use the method according to the invention for repairing defects in a stove-enamel layer within a multilayered enamel. One can distinguish at least two cases here:

1. Application of one of more bottom (substrate near) lacquer layer(s), optionally drying or hardening of this application, according to the invention, of powdered reparative lacquer (or aqueous powdered reparative lacquer slurry), melting and hardening of the (dried) powdered lacquer layer by NIR radiation, and optionally applying a covering lacquer with additional covering layers. For example, in the case of a defect to be repaired within a clear lacquer layer of a color-and/or effect-producing base lacquer/clear lacquer two-layered enamel, it is possible to first apply the color-and/or effect-producing base lacquer layer consisting of a base lacquer covering agent on the defect to be repaired in the stove-enamelling, optionally followed by exposing to air and/or stoving, then a powdered clear lacquer is applied, melted, and hardened by NIR radiation.

2. Application, according to the invention, of a powdered reparative lacquer (or a powdered reparative lacquer slurry), or application by melting and hardening of the (dried) powder enamel by NIR radiation with additional covering layers. For example, in the case of a defect to be repaired within a filler layer, it is filled with a powdered filler, which is then melted and hardened by NIR radiation before, for example, applying a coating enamel with base lacquer and clear lacquer. For example, the application of the coating enamel with base lacquer and clear lacquer can be carried out in the context of the first enamelling or in the context of a reparative enamelling on the finished object with a first enamelling. Another example concerns a defect to be repaired within a clear lacquer layer of a color-and/or effect-producing base lacquer/clear lacquer two-layered enamel. Here, one can apply a powdered lacquer to the defect that is ready to be repaired, for example, a defect that has not yet been polished down to the base lacquer layer or deeper, with such a powdered lacquer then being melted and hardened by NIR radiation.

The method according to the invention allows the reparative enamelling of defects in a stove-enamel, in particular using stove-enamels prepared using powdered lacquers. The above-described drawbacks of the state of the art can be prevented. The method is appropriate for an improved enamelling of series-lacquered, industrially manufactured objects, and particularly well suited for repairing defects within powdered lacquer layers produced in the context of car or car-part series enamelling, in particular powder covered and powdered clear lacquer layers.

Example

On a car hood with a typical series enamelling structure made of a cathodically formed base coat, filler, base lacquer and subsequent powdered clear lacquer layer, a dirt particle is located within the powdered clear lacquer layer.

The dirt particle is eliminated by polishing, without penetrating into the base lacquer layer. The result is an approximately 0.5-cm^2 defect that is ready for repair in the powdered clear lacquer layer. The area to be repaired is delimited from the defect-free surface by applying an adhesive heat-resistant film.

Onto the defect that is ready to be repaired, the same powdered clear lacquer as the powdered clear lacquer used to prepare the first enamel is applied by electrostatic spraying.

At a separation distance of 100 mm from the defect that has been coated with the powdered clear lacquer, an NIR emitter from the Industrie SerVis Company is positioned. The radiation is carried out for 8 sec and with a power of 400 kW/m^2, within which time the powdered clear lacquer melts and completely hardens.

Subsequently, the covering film is removed, with the repaired site being polished over a small surface area using a commercial polishing paste.

Claims

1. Method for repairing defects in a stove-enamel, characterized in that the defect, which has been prepared for the reparative enamelling, is coated with a powdered lacquer coating agent or an aqueous powdered lacquer slurry, with the applied powdered lacquer then being melted and hardened by radiation with near infrared radiation (NIR).
2. Method according to Claim 1, characterized in that it is carried out for repairing defects within stoved covering layers prepared from powdered lacquers.
3. Method according to Claim 1 or 2, characterized in that it is carried out for repairing defects within stove-enamels applied to cars and parts thereof.
4. Method according to one of Claims 1-3, characterized in that it is carried out for repairing defects in exterior, visible, stoved clear lacquer layers.
5. Method according to one of Claims 1-4, characterized in that the defects are prepared for the reparative enamelling, in particular by polishing, milling, or working the defects with a laser and/or cleaning.
6. Method according to one of Claims 1-5, characterized in that the radiation is carried out with NIR radiation in the wavelength range of 760-1500 nm.
7. Method according to one of Claims 1-6, characterized in that NIR emitters that can emit surface, line, or point-shaped focused radiation are used, to adapt to the defect to be repaired.
8. Method according to one of Claims 1-7, characterized in that the NIR radiation is carried out with conventional heat sources.
9. Method according to one of Claims 1-8, characterized in that it is carried out with a powdered lacquer or an aqueous powdered lacquer slurry, which has the same solid-matter composition as the lacquer used for the preparation of the stove-enamel layer have the defects to be repaired.

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